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Evaluation of the corrosion behaviour of potential plutonium wasteforms under conditions relevant for geological disposal

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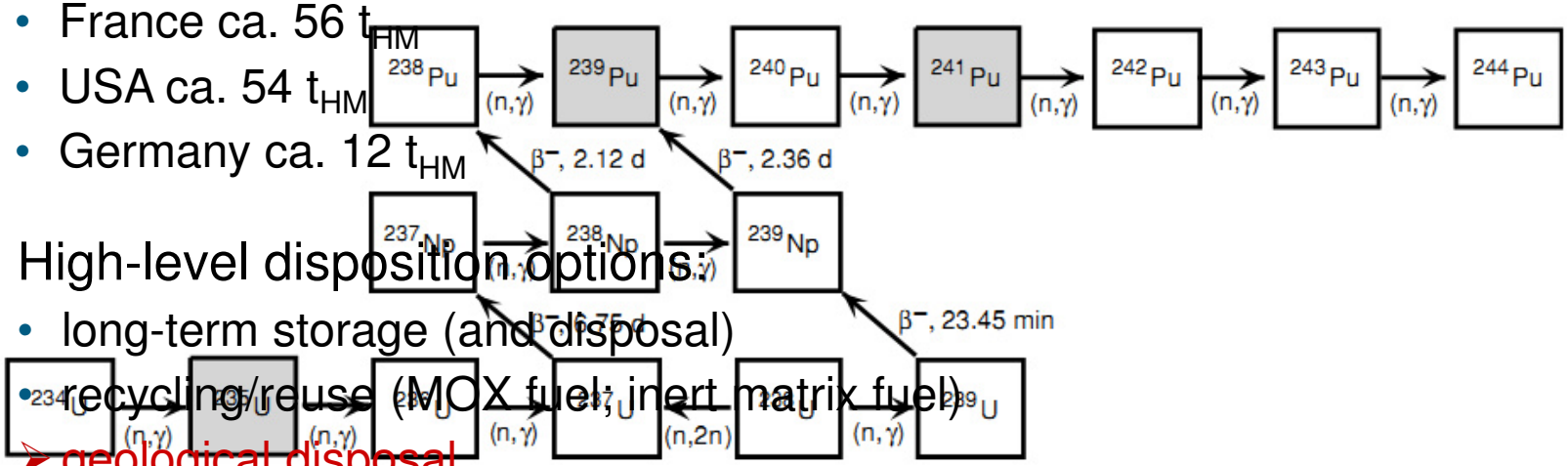
Background

- Plutonium (Pu)
  - forms in reactors using U-based fuels by various nuclear reactions (mainly n, γ)
  - separated during spent fuel reprocessing (e.g. PUREX process) and stored mainly as calcined PuO_2
  - isotopic composition variable depending on reactor type and fuel burn-up (predominantly Pu-239 and Pu-240)
- Stocks of separated civilian plutonium (2010)
  - UK ca. 92 t_{HM} (as of 31/12/2012)
  - France ca. 56 t_{HM}
  - USA ca. 54 t_{HM}
  - Germany ca. 12 t_{HM}
- High-level disposition options:
  - long-term storage (and disposal)
  - recycling/reuse (MOX fuel; inert matrix fuel)

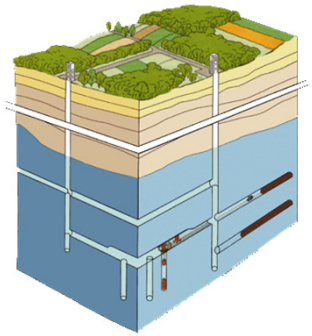


➢ geological disposal

Wasteform issues for Pu disposal

Conversion

Geological Disposal



- waste loading
- chemical stability
- radiation stability
- He build-up
- thermal stability

- chemical flexibility
- criticality control
- safeguards
- fabrication route
- technological maturity

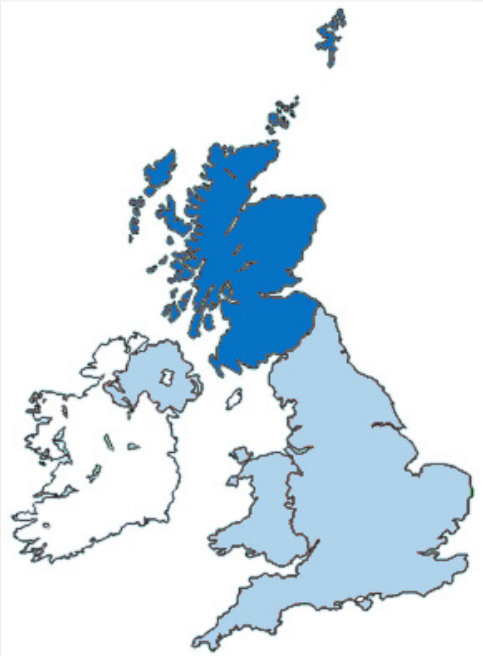
➢ Safety case issues for geological disposal
- long-term durability of Pu wasteforms
- long-term radionuclide release from Pu wasteforms under repository relevant conditions

Scope & Objectives

- NDA RWMD responsible for the implementation of geological disposal of higher activity wastes in the UK
- wastes to be managed through geological disposal:
  - HLW, ILW, LLW (if unsuitable for LLWR)

  and potentially
  - spent fuel (SF)
  - ➢ separated civil plutonium
  - uranium (DNLEU)

  if declared as wastes



- Objectives:
  - evaluation of performance and long-term behaviour of potential Pu wasteforms under repository conditions relevant for the UK
  - elicitation of corrosion rates / Pu release rates under disposal conditions
  - ➢ support decisions on Pu disposal in the UK

Potential Pu wasteforms

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Glasses

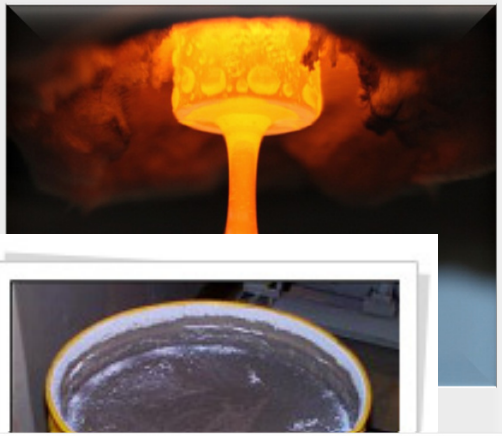
Glass ceramics

Ceramics

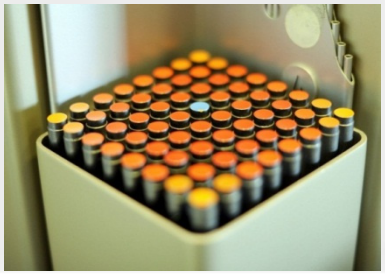
Storage MOX

Cement

- Borosilicate glasses
  - lanthanide borosilicate
  - lead borosilicate
  - calcium borosilicate
- Alkali-Tin-Silicate glasses
- Phosphate glasses
  - iron phosphate
  - aluminium phosphate



- Low-specification (“storage”) MOX
  - MOX fuel not destined for reactor usage (fabricated by established technology)
  - reduced technological specifications
  - higher Pu load compared to commercial MOX
  - fuel rods / fuel assemblies mixed with SF (radiation barrier)



Evaluation of wasteform performance

- Key issues:
  - long-term radionuclide release under realistic repository conditions (for derivation of source terms for PCSA)
  - wasteform stability/integrity over geological time scales (effects of radiation damage, helium build-up)
  - criticality control

  ? Sufficient information available for the assessment of the long-term behaviour and performance of the wasteforms ?

- Key controls of wasteform performance:

- intrinsic (wasteform)
  - plutonium loading
  - mode of Pu incorporation
  - chemical/mineralogical composition
  - radiation tolerance
  - mechanical stability

- extrinsic (repository environment)
  - hydrogeology (advective vs. diffusive flows)
  - geochemical conditions (pH, E_H, T, I, A^+, B^-, …)
  - microbial activity

  ➢ dependent on repository design (EBS) and host rock

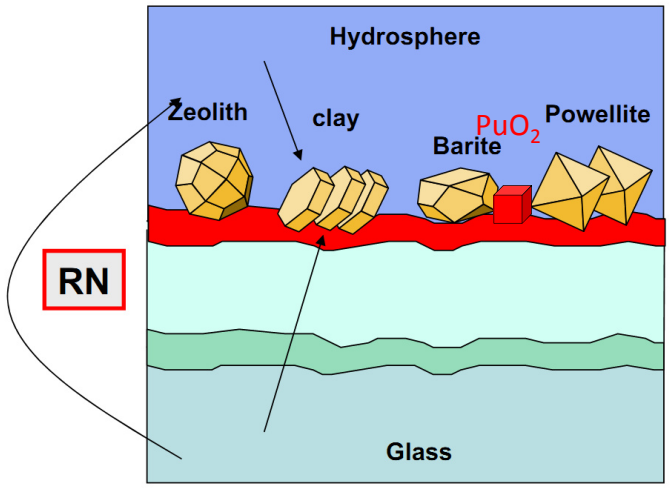
Glass wasteforms for Pu

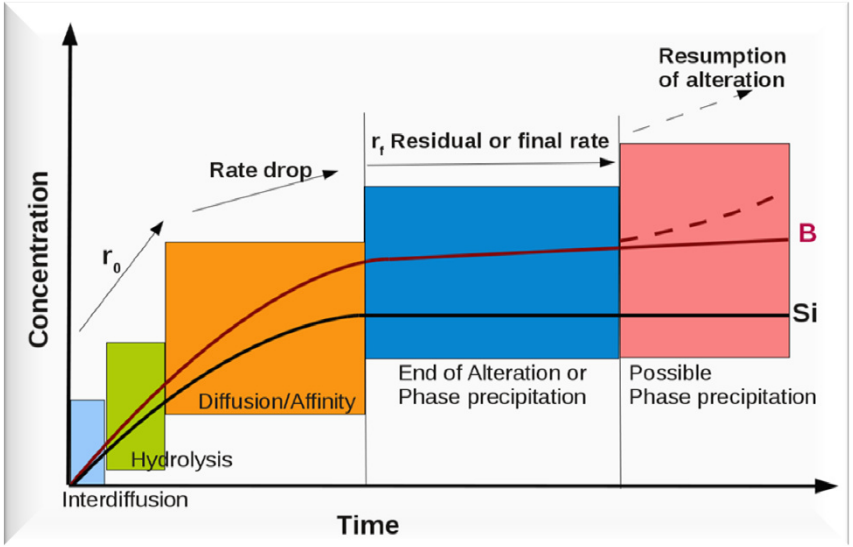
- comparatively few studies on the durability of Pu waste glasses compared to HLW glasses
- focus mainly on borosilicate / LnBS glasses
- leaching experiments mainly with standardised tests (MCC, PCT) using deionised water, mainly with surrogates (Ce, Hf), few long term tests

➢ leaching rates for Pu (or surrogates) significantly lower than for glass matrix elements (e.g. B, Si, etc.)

➢ Pu (and surrogates) retained in secondary phases

➢ no effect of radiation dose on Pu release observed for borosilicate glass





Ceramic wasteforms for Pu

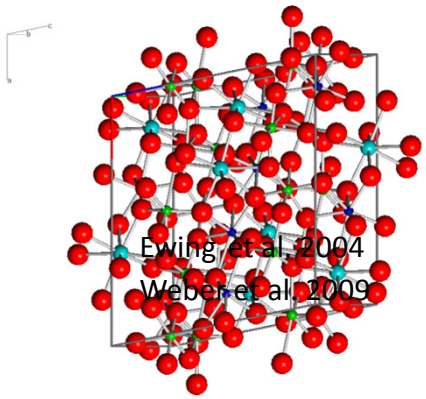
- investigations performed on various polyphase and singlephase ceramics for actinide/Pu immobilisation
- leaching experiments often with standardised tests (MCC, PCT) using deionised water or under acidic conditions, often with surrogates (Ce, Hf), long-term tests rare

➢ leaching rates are orders of magnitude lower compared to glasses with rates for Pu (and surrogates), Ti and Zr often ~10^{-5} g m^{-2} d^{-1} or less

➢ data for ZrO_2-based pyrochlores are rare

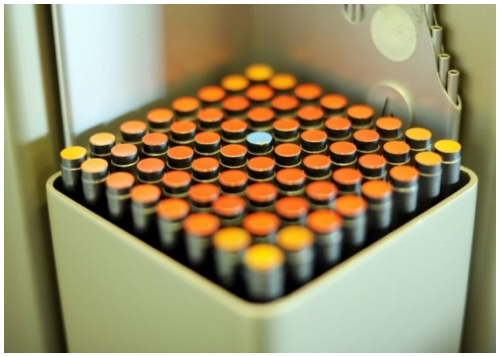
➢ different response to self irradiation

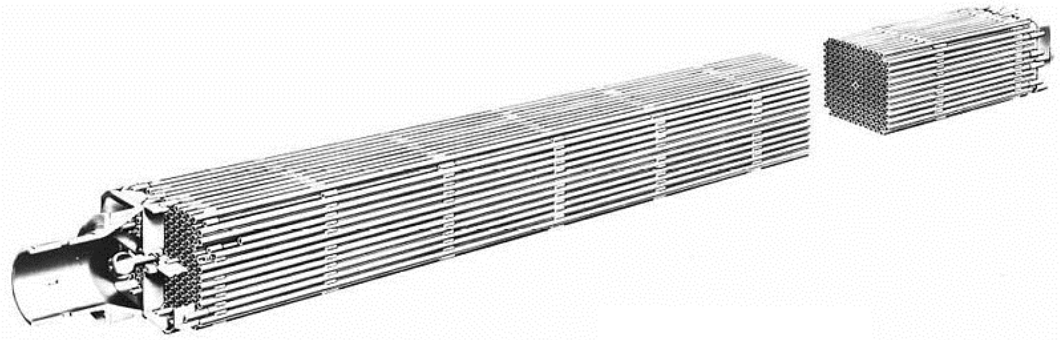
- no amorphisation of monazite and Zr-pyrochlore
- no effect of radiation dose on Pu release observed for zirconolite



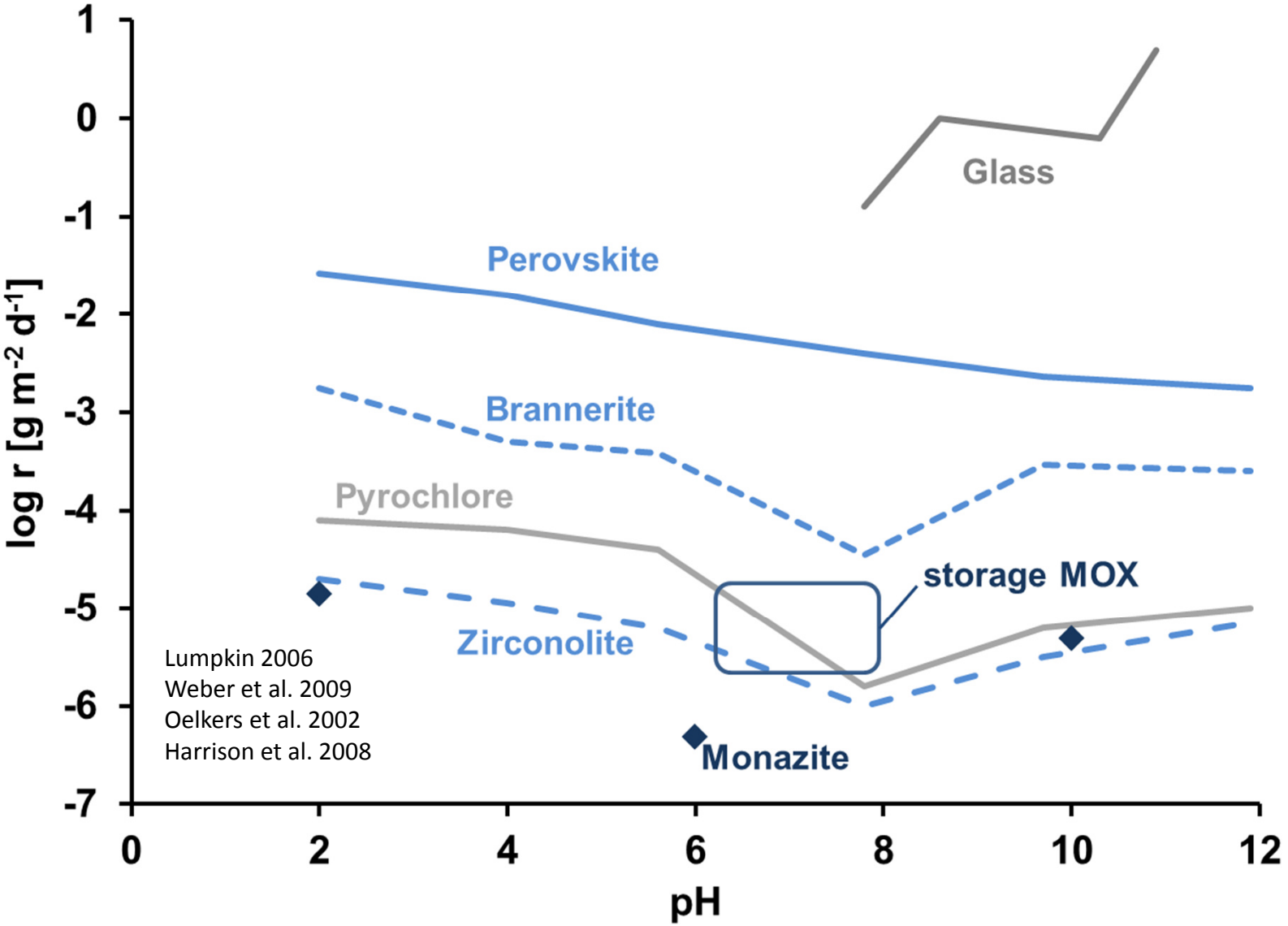
Storage MOX as a wasteform

- concept has received considerably less attention than immobilisation of Pu in glasses and/or ceramics
- very limited information on wasteform behaviour available
- ➢ short term static leaching tests in deionised water, granitic water and carbonated water suggest leaching rates around 10^{-5} g m^{-2} d^{-1}
- ➢ Pu leaching rates under reducing conditions lower than for uranium
- ➢ high durability under reducing (long-term) conditions in a GDF inferred

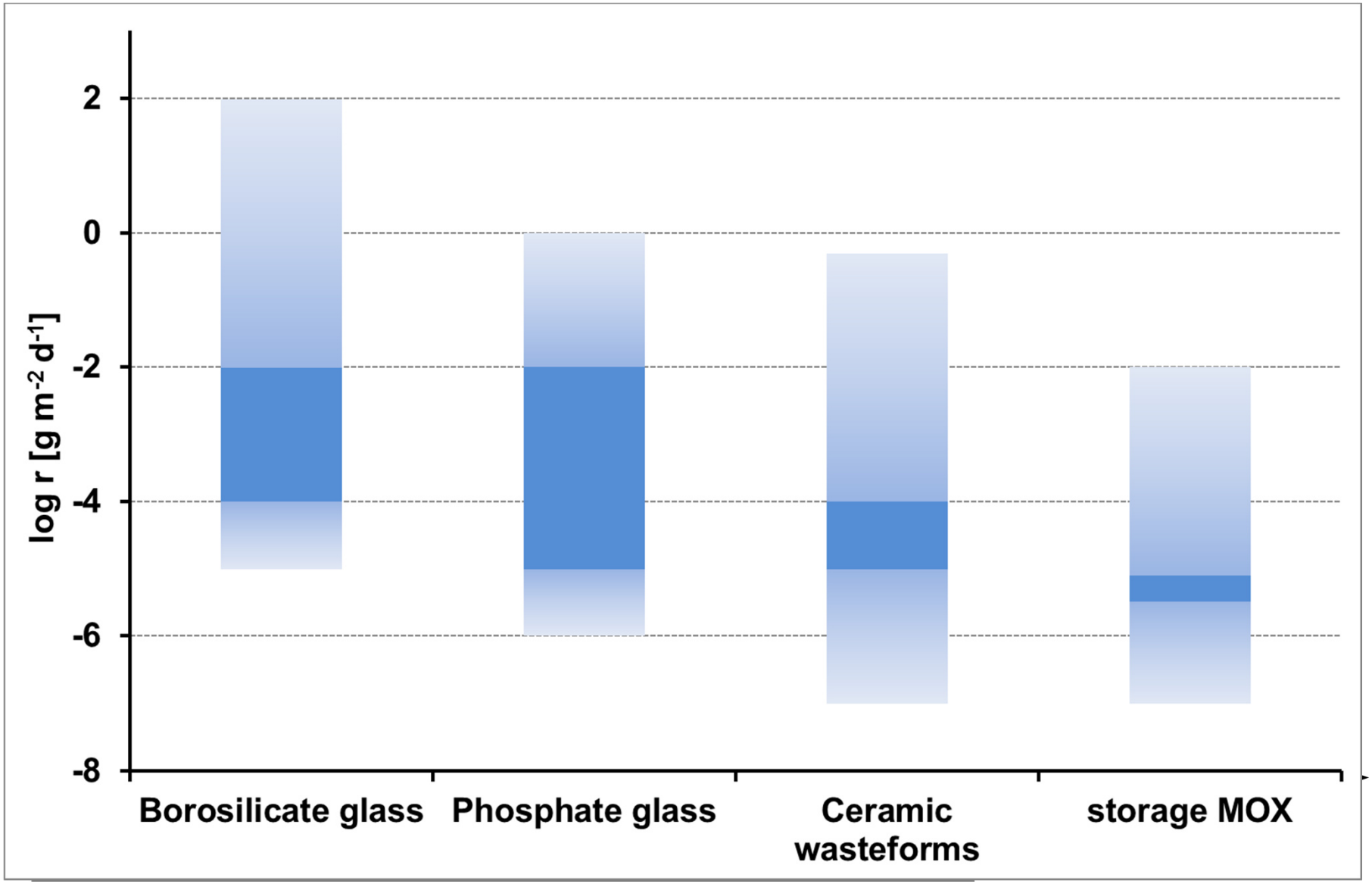




Performance under disposal conditions



Elicitation of dissolution rates for PCSA



Conclusions & Outlook

- High level review of the performance of candidate wasteforms for Pu disposal under repository conditions:
  - available information on the wasteforms is highly variable focussing mainly on ceramics and glasses
  - each wasteform offers distinct strength and weaknesses
  - ceramic wasteforms promising with respect to durability/radionuclide release
  - detailed understanding of relevant processes that govern radionuclide release from the wasteforms and total systems behaviour seems to be still missing
  - compared to assessments of realistic source terms for HLW/SF disposal, information on Pu wasteforms is rather limited

- Bounding values for wasteform corrosion rates and Pu release rates under repository conditions were derived from experimental data and analogue evidence
- However:

  more realistic source terms would require systematic studies regarding:
  - Pu wasteform dissolution and radionuclide release rates under realistic conditions
  - characterisation of secondary phases formed during Pu wasteform corrosion
  - effects of radiation damage on Pu wasteform performance/durability

The End

Thanks to

- NDA RWMD: for funding this project
- The Audience: for kind attention

Questions???